



Electrolyte depletion control laws for lead-acid battery discharge optimisation



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HIGHLIGHTS

- We maximise both the discharge current and duration.
- Battery control prevents electrolyte depletion.
- Battery controls are 1) proportional controls and 2) integrated past controls.
- The controls are exponentially stabilising controls.

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ABSTRACT

The technique described in this paper balances the power and energy withdrawn from a battery in galvanostatic discharge control that aims for stabilisation of the electrolyte concentration above the depletion level. This aim is achieved with relatively simple proportional feedback controls that are exponentially stabilising controls for a simple diffusion process that is the core part of battery processes. Although the full mapping of the proposed controls to state is rather complex, it has shown that the transformation works. In practice, these controls can be approximated either with the integrated past controls or with a simple exponential function that depends on a few parameters adjusted to the electrochemical processes in a battery under consideration. The battery control is tested in simulation on a detailed model developed for a lead-acid electrochemical cell.

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1. Introduction

Backup batteries are a source of power in many energy systems. On demand, the batteries should supply the largest current possible while withdrawing the maximum amount of chemical energy. These objectives are contradictory and hence difficult to achieve because ion depletion of the electrolyte emerges, always, when the discharge current is large.

This paper maximises both the discharge current and duration. The objectives are achieved using appropriate boundary controls that stabilise the depletion process. These controls are proportional feedback controls that, in a practical application, can be either approximated with a simple time-dependent function with a few parameters adjusted to a battery or represented as integrated past controls. The proposed depletion process controls are asymptotically stabilising controls; to some extent, they can be compared with a simpler potentiostatic control if the reference point for the

desired voltage is selected in a close and safe distance from the cut-off voltage.

Widespread current interest in discharge control arises from safety issues in powerful lithium ion batteries that should be controlled in the dependence on the state of electrochemical processes in batteries. Monitoring and control of the electrochemical processes in batteries would allow their safe use. For example, the lack of safe control is a primary obstacle for use in the important application area of the automotive sector.

In contrast to lithium ion batteries, lead-acid batteries are well understood and are an excellent facility for simulation of cell controls.

Significant research efforts related to modelling of lead-acid batteries have been carried out by several groups over a long period. Although numerous other and significant contributions to the topic have been made, the work of Newman and Tiedemann [1], Hiram Gu, Nguyen, White [2], Nguyen, White, Hiram Gu [3], Gu, Wang, Liaw [4], Newman and Thomas-Alyed [5], Boovaragavan et al. [6], Cugnet et al. [7], Kashkooli et al. [8] are some that should be mentioned, as they have strongly influenced the work behind

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this paper. We also build on work related to the modelling of maintenance-free, valve-regulated lead-acid batteries by Berndt [9], Tenno et al. [10–13].

The control research of batteries at the electrochemical cell level has seen less attention in the literature. However, the depletion control has been considered in other electrochemical processes (electrodeposition, via fill) using deterministic [14–17] and stochastic [18] models.

2. Battery model

The lead-acid batteries can be modelled in single dimension as a sandwich of electrochemical cell represented in Fig. 1. The model of the cell is well established and varies only slightly in the literature. In this work, one of the models [2] is selected for the basis and modified for the computational and control needs. The modified model is explained in Sections 2.1–2.7.

The concern of this paper is a discharge process that can be explained with the four primary reactions in the spatial domain (regions 1–4 in Fig. 1) and with the boundary conditions at the collector (centrum) $x = 0$ of positive electrode and at the collector $x = l_4$ of negative electrode. In discharge, the secondary reactions (the water decomposition and oxygen/hydrogen recombination and the double-layer effect) are insignificant [19–21]; we omit them.

For brevity and simpler understanding, the model is explained in conceptual terms. All the details required for building of the computational model in the 4 subdomains and on/at the 5 boundaries are explained and given in the Appendix, Table 1. For the computational needs, the model can be extended most simply if the interested reader starts from the model in the literature [2] and then updates this model using our modifications explained in Section 2.7.

The battery model includes many physical processes. For streamline reading and brevity, the explanation of most symbols (that are more or less standard) is omitted from the text, and symbols along with their explanation are compiled in the Appendix, Table 2. The parameters used in simulation are taken either from the literature [6–8] or from our previous study [10,11]; they are given in Table 1.

2.1. The positive electrode

The primary processes (1)–(3), (5) in the positive electrode (region 1 in Fig. 1) are coupled with each other and with the related processes (6), (8)–(11) as follows.

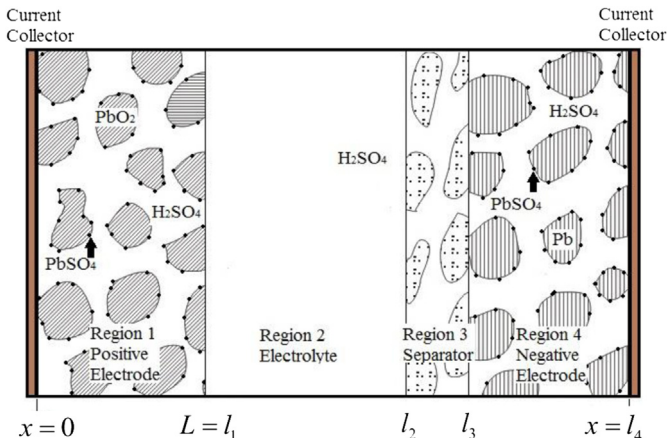


Fig. 1. The electrochemical cell represents a lead-acid battery in a single dimension.

Model of the porosity of electrode

$$\frac{\partial \varepsilon}{\partial t} = D_e \frac{\partial^2 \varepsilon}{\partial x^2} + (V_{\text{PbSO}_4} - V_{\text{PbO}_2}) \frac{A_j}{2F} \quad (1)$$

Ohm's law in solid porous matrix

$$\delta_e \frac{\partial \phi_s}{\partial t} = \frac{\partial}{\partial x} \left(\varepsilon^{\beta_1} \sigma_{\text{PbO}_2} \frac{\partial \phi_s}{\partial x} \right) - A_j \quad (2)$$

Ohm's law in electrolyte

$$\delta_e \frac{\partial \phi_l}{\partial t} = \frac{\partial}{\partial x} \left(\varepsilon^{\beta_2} \kappa \frac{\partial \phi_l}{\partial x} \right) - \frac{RT}{F} (1 - 2t_0^+) \frac{\partial}{\partial x} \left(\varepsilon^{\beta_2} \kappa \frac{\partial \ln(c)}{\partial x} \right) + A_j \quad (3)$$

In Eq. (3), the conductivity coefficient $\varepsilon^{\beta_2} \kappa$ depends on the porosity [1,15] and on the concentration of the electrolyte $\kappa(c)$; we use an empirical formula in Table 1 for the latter relationship.

The electric field and diffusion potential drives the ion current in the electrolyte [5].

$$\frac{i_l}{\varepsilon^{\beta_2} \kappa} = -\frac{\partial \phi_l}{\partial x} + \frac{RT}{F} (1 - 2t_0^+) \frac{\partial \ln c}{\partial x} \quad (4)$$

In Eq. (4), the first component on the right is the ion migration-related current in the electric field, due to the conductivity of electrolyte and the second component is the diffusion-related current, due to the concentration gradient that creates diffusion potential, which prevents substantial separation of binary charges with different diffusivities (slower and faster).

Mass balance in the electrolyte depends on three main processes: diffusion, convection and electrode kinetics, shown in the same order from right to left in Eq. (5).

$$\varepsilon \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} D_e \varepsilon^{\beta_2} \frac{\partial c}{\partial x} + u_v \frac{\partial c}{\partial x} + \left((3 - 2t_0^+) (1 - cV_e) + 2cV_o \right) \frac{A_j}{2F} \quad (5)$$

Here the diffusivity coefficient $D_e \varepsilon^{\beta_2}$ depends on the porosity of the electrode [1,5] and on the concentration of the electrolyte $D(c)$; we use an empirical formula in Table 1 for the latter relationship.

For a large discharge current, the convection of the electrolyte out of the electrode is substantial [8]; its dependence is on the variable porosity as the volume average velocity of convection [1].

$$u_v = (V_{\text{PbSO}_4} - V_{\text{PbO}_2} - (3 - 2t_0^+) V_e + 2V_o) \frac{i_l}{2F} \quad (6)$$

Conservation of charge requires that the charge entering the solution phase equals the charge leaving the solid matrix phase. Hence, the current densities for solid i_s and liquid i_l phases satisfy the continuity Eq. (7).

$$\frac{\partial i_l}{\partial x} + \frac{\partial i_s}{\partial x} = 0 \quad (7)$$

The total current transferred from the liquid phase to the matrix phase is equal to the net rate of electrochemical reaction per unit volume of electrode.

$$\frac{\partial i_l}{\partial x} = A_j \quad (8)$$

The electrochemical reaction is a specific property that depends on electrode kinetics. In this work, the two-directional Butler–Volmer equation (9) is applied to describe the electrode kinetics

$$j = i_0 \frac{c}{c_{\text{ref}}} \left(\exp \left(\alpha_a \frac{F}{RT} \eta \right) - \exp \left(-\alpha_c \frac{F}{RT} \eta \right) \right) \quad (9)$$

In Eq. (8), Aj is the volumetric current density and j is the current density that due to the electrode kinetics (9) depends on the surface overpotential $\eta = \phi_s - \phi_l - E_{\text{PbO}_2}$ and that in turn depends on the equilibrium potential E_{PbO_2} that again depends on the standard equilibrium potential U_{PbO_2} and on the acid concentration as shown in the modified Nernst equation (10). In contrast to the conventional dilute solution assumption, the electrolyte in batteries is concentrated. For this effect, the conventional Nernst equation is combined with the linear function bc that compensates for the dilute solution error in (10).

$$E_{\text{PbO}_2} = U_{\text{PbO}_2} + \frac{RT}{2F} \log \left(\frac{c}{c_{\text{ref}}} \right)^{\beta_4} + bc \quad (10)$$

The electrochemical reaction Aj at the electrode depends on the surface area A in the porous electrode, that in turn depends on $a = a_{\text{max}} \theta^{\beta_3}$ the state of charge θ that can be computed either by integration of Aj over time, or in a simpler case, expressed through the porosity [2]

$$\theta = \frac{\varepsilon - \varepsilon_{\text{min}}}{\varepsilon_{\text{max}} - \varepsilon_{\text{min}}} \quad (11)$$

In this model, all dynamic processes (1)–(3), (5) are coupled with reaction-related processes (8)–(11) and with the electric field process (4) and diffusion potential-related process (6).

2.2. The reservoir and separator

The electrochemical reaction is absent in the reservoir (region 2) and separator (region 3 in Fig. 1). The missing reaction term $Aj = 0$ simplifies the model there to the diffusion–convection model. Porosity is the known constant in the separator and 1 in the reservoir. Also, the equation for potential in the solid phase is absent in the reservoir and separator, but the equation for potential in the liquid phase is still present in the form of the diffusion–convection equation.

2.3. The negative electrode

The model for a negative electrode (region 4) is similar to the positive electrode, except its own parameters for this region (Table 1) should be applied and also slightly different Eqs. (12) and (13) for electrolyte mass balance should be used.

$$\varepsilon \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} D \varepsilon^{\beta_2} \frac{\partial c}{\partial x} + u_V \frac{\partial c}{\partial x} + (1 - 2t_0^+) (1 - cV_e) \frac{Aj}{2F} \quad (12)$$

Since the material of electrodes is different in the positive ($\text{PbO}_2/\text{PbSO}_4$) and negative (Pb/PbSO_4) electrodes, the conservation of volume is arranged differently in the positive (6) and negative (13) electrodes.

$$u_V = - \left(V_{\text{PbSO}_4} - V_{\text{Pb}} + (1 - 2t_0^+) V_e \right) \frac{i_l}{2F} \quad (13)$$

Dimensions of the electrochemical cell are important; they should be specified in dependence on a specific type of battery that is a weakness of the current approach (model related). For dimensions used in simulation, see Table 1.

2.4. The outer boundary conditions on collectors

The insulation condition (zero flux) is assumed at/on the collector of a positive electrode for all processes except for the solid material potential that satisfies the Neumann condition (14).

$$\varepsilon^{\beta_2} \sigma_{\text{PbO}_2} \frac{\partial \phi_s}{\partial x} \Big|_{x=0} = i_{\text{app}}(t) \equiv u(t) \quad (14)$$

Here $i_{\text{app}}(t)$ is the applied current; this is a control $u(t)$ still to be found.

The zero flux condition is assumed also at/on the collector of negative electrode for all processes except for the solid material potential that satisfies the homogeneous Dirichlet condition (15).

$$\phi_s(t, L) = 0 \quad (15)$$

As the negative electrode is grounded, all the potentials are understood as the shifted potentials with the value $-U_{\text{Pb}} = -0.336$ of standard equilibrium potential on negative electrode (versus H_2 electrode).

2.5. The inner boundary conditions

There are inner boundaries between regions 1–2, 2–3, 3–4 in Fig. 1. The neighbouring subdomain fluxes must match, and, as the consequence, the continuity condition is applied in between the regions for the liquid potential and for the electrolyte concentration. The discontinuity condition (zero flux) is applied for the porosity and for the solid matrix potential.

2.6. The initial conditions

The initial condition for porosity in electrodes is given by the constant ε_{max} for a fully charged battery in Table 1. The electrolyte initial concentration is given by the reference concentration c_{ref} that, in other words, is the electrolyte concentration in a new battery. The initial potential on the positive electrode is taken equal to the standard cell voltage $U_{\text{PbO}_2} - U_{\text{Pb}}$ and zero on the negative electrode. The initial potential of liquid is given by the equilibrium potential of (10), computed by the reference concentration. This gives a slightly more positive potential than the standard equilibrium potential U in Table 1.

2.7. The modified model

The model presented in this paper has a large common part with the model in Ref. [2]. We modified the latter model for the computational and control needs in several ways:

1. The original hyperbolic equation [2] for porosity is perturbed with a small diffusivity D_e that results in parabolic Eq. (1).
2. The original first order equation [2] for Ohm's law in solid matrix and Ohm's law in electrolyte is differentiated spatially, and then the elliptic equation is approximated with the parabolic equation using a fast dynamics. For implementation of fast dynamics, the time derivative is scaled with a small factor δ_e in Eqs. (2) and (3).
3. The gradient of current in the liquid phase is replaced with the net rate of electrochemical reaction per unit volume of electrode (8) that results in the Eqs. (1)–(3), (5).
4. The continuity Eqs. (7) and (4) for ion current in the electrolyte is utilised to eliminate the current in both phases that results in the balance between the number of unknowns 4 and equations 4 necessary for solution of the model.

This modification is required for the regularity and stability of the computational model. In this work, the artificial diffusivity $D_e = 10^{-20} \text{ (m}^2 \text{ s}^{-1}\text{)}$ and the time-scaling factor $\delta_e = 10^{-20}$ (dim less) are small. They improve regularity of the computational model that simulates almost identical processes to the original model in the literature (i.e. the small parameter effect).

This is not difficult to extend the model (1)–(15) for 4 sub-domains and 5 boundaries. Also, extension of the model to higher dimensions does not create principal problems, but computationally the 2D and 3D models are more time consuming to solve.

2.8. Software packages

Various computational models have been implemented in software packages, like Comsol Multiphysics 4.0 and later versions. An early version of the model has been developed and implemented in the domestic software by A. Tenno [11]. The current version of the computational model is implemented under Comsol Multiphysics 3.5a. Also, the model by Kashkooli et al. [8] is similar and implemented under Comsol Multiphysics 3.5a.

2.9. Abstract ODE system

The battery model can be represented as an abstract ODE (original differential equation) system (16).

$$\frac{dz}{dt} = A(t, z)z(t) + R(t, z) \quad (16)$$

In Eq. (16), $z = [\varepsilon \phi_s \phi_l c]^T$ is the state vector; $A(t, z)$ is the second and first order nonlinear, non-degenerated, unbounded operator; $R(t, z)$ is the unbounded non-Lipschitz function that represents $R = B(Aj)(t, z)$ the nonlinear electrode kinetics Aj and the constants in vector B specified in correspondence to the Eqs. (1)–(3), (5). This system (16) satisfies the mixed homogeneous Neumann boundary condition for all processes except for the potential on the collector of the positive electrode, where the non-homogeneous Neumann boundary condition (14) holds for control $u(t)$ exercised through the boundary and except for the potential on the collector of the negative electrode, where the homogeneous Dirichlet boundary condition (15) holds. The spatial domain consist of four sub-domains, where the reaction terms are either zero (separator, reservoir) or nonzero (electrodes). The continuity condition holds on the inner boundaries for ϕ_l , c and the discontinuity (zero flux) condition holds for ε , ϕ_s .

This system (16) is not covered by the crucial assumptions of the general theory for abstract ODEs [22–24] that is mostly developed for linear systems. The Lipschitz continuity and boundedness of the reaction term are the crucial assumptions of the general (nonlinear) theory that are not satisfied in (16). In addition, the process (16) is discontinuous on interior boundaries; on outer boundaries, it must be homogenised for the theoretical treatment, and this creates new difficulties if the unknown boundary controls (non-smooth in general) will be lifted in the domain.

Because of so many dissolved difficulties, direct application of the ODE system (16) seemed hardly possible. For control of the opposite, we need a simpler model that is still relevant to the essence of battery processes. Such a model will be proposed in Section 4 and applied with developed controls on the detailed battery model in Section 5.

3. The control problem

A battery loading must balance two objectives: maximise the discharge current and energy withdrawn from the battery. These objectives are recasted in a performance index (17) that depends on two control variables: the discharge stopping time and discharge current.

$$E = \sup_{\tau, u} \int_0^{\tau} |u(t)| dt \quad (17)$$

The twofold aim in (17) can be elucidated with two non-optimal strategies.

1. If the discharge current is small $u = u_0$ (non-optimal), then the discharge time is large, say $\tau(u_0) \approx \infty$ (optimal), and almost all the chemical energy in a battery can be released.

$$E_0 = \int_0^{\infty} |u_0| dt < E \quad (18)$$

2. In contrast, if the discharge current is large $u = u_0^{-1}$ (optimal), then the discharge time remains small, say $\tau(u_0^{-1}) \approx \tau_{\text{stop}}$ (non-optimal), and only a part of the chemical energy can be pulled out.

$$E_1 = \int_0^{\tau_{\text{stop}}} |u_0^{-1}| dt < E \quad (19)$$

Neither of these controls is optimal simultaneously.

The performance index (17) represents a double-minded aim of optimal stopping and energy maximisation that can be reformulated as a single-minded energy maximisation aim if the integrant under (17) is modified, and the process model is modified in a way that they are zeroes if the concentration in the positive electrode reaches zero or state of charge reaches zero in either electrodes and due to the modified model they stay there forever. The performance index (17) with two control variables is equivalent to the performance index (20) with single control variable.

$$E = \sup_u \int_0^{\tau_D} |u(t)| dt = \sup_u \int_0^{\infty} |u(t)|_D dt \quad (20)$$

Here τ_D is the first moment when the process (c, θ) exits the domain $D = (c, \theta : c > 0, \theta > 0) \subset R^2([0, \infty), (0, 1))$, $|u(t)|_D$ is the modified function equal to the original function $|u(t)|_D = |u(t)|$, if $(c, \theta)(t, x) \in D$, and zero otherwise.

Theoretically, the performance index (20) can be maximised with respect to the system (16); however, in practice, such a solution to the optimal control problem is difficult to find. Our chances to solve the problem are better if we remember that in backup systems, one is not very interested in the limited stopping time when some proportion of chemical energy stays unused. In backup systems, we are interested in control that is relevant to the unlimited (infinite) stopping time as in (20). A balance between the unlimited stopping time and applied large current should be found. This problem is solved at first on a simplified model in Section 4 and then applied to the detailed battery model in Section 5.

The idea for the solution comes from the main goal of control that aims to maximise energy in a good balance with the depletion process. It is anticipated that the maximal current is obtained when the acid concentration in the positive electrode is driven to such a level that mass transfer of the acid ions to the collector is maximised, but the surface of the collector is still not depleted of acid ions. If depletion would occur, then the current ends through the positive electrode that is more sensitive to the starvation of ions. Although the control problem is a maximisation problem with constraint that keeps the acid concentration above zero, a much simpler regulator problem is solved in Sections 4 and 5.

From the control viewpoint, the most essential part of the battery model is the diffusion process in the positive electrode that should be controlled sensibly through the boundary. Such control will be found next.

4. Diffusion process control

In this section, a simple diffusion process that represents a simplified diffusion in the positive electrode is controlled. In general, this model includes uncertainties of the ignored processes in batteries and therefore, is the stochastic model. In the case of additive noises, the averaged diffusion process coincides with the noise-free process (21)–(24)

$$c(0, x) = c_{\text{ref}} \quad (21)$$

$$\frac{\partial c(t, x)}{\partial t} = D \frac{\partial^2 c(t, x)}{\partial x^2} \quad 0 \leq x \leq L, t > 0 \quad (22)$$

$$D \frac{\partial c(t, x)}{\partial x} \Big|_{x=0} = \frac{i_{\text{app}}(t)}{2F} = u_1(t) \quad (23)$$

$$c(t, L) = c_{\text{ref}} \quad (24)$$

The electric current $i_{\text{app}}(t)$ is control $u(t)$ in (14), and the mass flux is control $u_1(t)$ in (23). These are basically the same controls $u(t) = 2Fu_1(t)$ in different units A m^{-2} and $\text{mol (m}^{-2} \text{s}^{-1})$, correspondingly.

The regulation errors induced by the noises in the stochastic system are bounded; they are analysed in the cases of finite dimensional Wiener process in Ref. [18] and cylindrical Wiener process in Ref. [25].

4.1. The boundary control

If one stabilises the acid concentration at the collector of the positive electrode at the desired level as the following proportional control does

$$u_1(t) = -K_P(c(t, 0) - c_d) \quad (25)$$

this brings the initial concentration of electrolyte close to the desired level c_d . This can be shown strictly using system (21)–(24) that the proportional boundary control (25) satisfies (26).

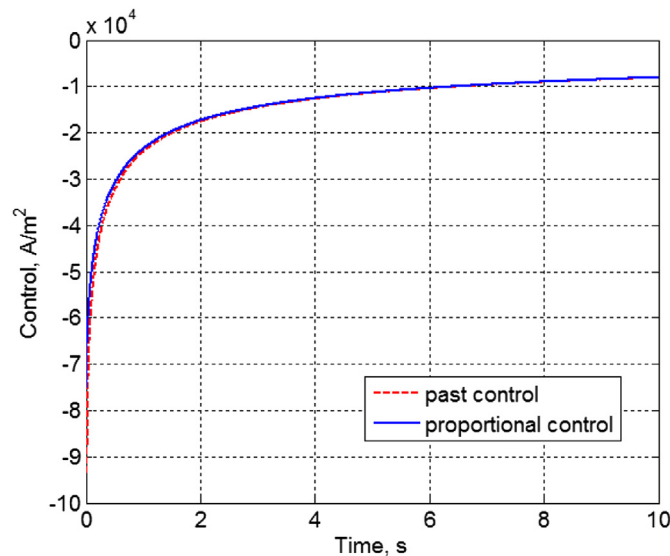


Fig. 2. The proportional controls (25) and past controls (30) are almost identical except very initially.

$$c(t, 0) - c_d \rightarrow \frac{D}{D + K_P L} (c_{\text{ref}} - c_d) \equiv c_d^0 \quad (26)$$

If $D \ll K_P L$ the bias from the target c_d is small $c_d^0 \approx 0$; moreover, this bias can be eliminated entirely if a slightly lower reference point $c_s = c_d - c_d^0$ is aimed as in (27). Since the static error c_d^0 is constant (known), it can be removed effectively without integration of control errors.

$$u_1(t) = -K_P(c(t, 0) - c_d + c_d^0) \quad (27)$$

This control (27) is an exponentially stabilizing control.

4.2. The feed-forward control

The feed-back boundary control (25) (or (27)) can be expressed as the model-based feed-forward control (28) or (30) that does not require concentration measurements on the boundary. The control (28) reads

$$u_1(t) = -K_P(c_{\text{ref}} - c_d) \left(\frac{D}{D + K_P L} + 2K_P D \sum_{n=1}^{\infty} \frac{e^{-\mu_n^2 D t}}{LK_P^2 + K_P D + \mu_n^2 L D^2} \right) \quad (28)$$

In Eq. (28), μ_n are the roots of the transcendental Eq. (29).

$$\frac{D}{K_P} \mu + \tan(\mu \delta) = 0 \quad (29)$$

These roots can be found with the fixed point iteration method, which is a fast computing method: in this particular case, for example, the convergence to three-digit accuracy occurs in ca. 10 steps. The sequence of roots increases rapidly $\mu_n \rightarrow \infty, n = 1, 2, \dots$ so rapidly that the sum in (28) converges in ca. 50 steps.

For any gain $K_P > 0$ the system is stable. The lack of dynamics between the boundary concentration and current density in (25) makes the system stable provided that the system is stable in open loop, which is the case in any natural diffusion $D > 0$ process.

Proof outline (26)–(29). The change of variables and separation of variables techniques are applied on (21)–(24) and (25) to prove (26)–(29). For details, see Ref. [25].

In simulation (Section 6), we demonstrate that the control (27) preserves the same stabilising property in the case of batteries.

4.3. The past control

The proportional control (25) can also be expressed as in (30) in dependence on the past controls $u_1(\tau)$ that are available in a discharge process.

$$u_1(t) = -K_P(c_{\text{ref}} - c_d) - \frac{K_P}{\sqrt{\pi D}} \int_0^t \frac{u_1(\tau)}{\sqrt{t - \tau}} \left(1 + 2 \sum_{n=1}^{\infty} (-1)^n e^{-\frac{n^2 L^2}{(t - \tau) D}} \right) d\tau \quad (30)$$

The sum in (30) can be computed recursively and then integrated with the past controls. However, the dynamics that exist between the boundary concentration and current densities in the case of past controls (30) makes the system unstable for a large gain K_P . Here we phase a dynamic feedback. In the case of mild control with a relatively small gain, the system is still stable. In Fig. 2, the proportional control (25) is compared with the past control (30); if

$K_P = 10^{-4} \text{ m s}^{-1}$, the controls coincide rather well except initially for a short period that is insignificant in battery application, when $D = 2.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $L = 7 \times 10^{-4} \text{ m}$. The past controlled system loses its stability if the control gain is essentially larger: for example, if the gain is 10 times larger, the proportionally controlled system is still stable but not the past controlled system. Currently, the exact conditions for exponential stability of (30) are unidentified (the upper limit for K_P is unknown).

Similarly to controls, the controlled processes (Fig. 3) on the boundary are almost identical except initially. A relatively short period of discharge in Figs. 2 and 3 is shown by the purpose to demonstrate the small initial effect.

Proof outline (30). The change of variables, Laplace transform, Efros' theorem, convolution theorem and direct integration techniques are applied on (21)–(24) to prove (30). For details, see Ref. [25].

4.4. The discharge cost of boundary controls

Assume that a battery can be boundary controlled (still to be shown); then, for any moment $t \in (0, \infty]$, the electrode is not depleted $c(t, x) \in D$ and the current is not zero $|u(t)|_D = |u(t)|$ as far as the SOC is above zero in both electrodes, otherwise $|u(t)|_D = 0$. Integrating controls (25) under the cost function of (20), we maximise energy in the case of unlimited discharge time. The optimal cost reads

$$E = 2FK_P \left| c_{\text{ref}} - c_d \right| \left| \frac{D}{D + K_P L} + \sum_{n=1}^{\infty} \frac{2}{\mu_n^2} \frac{K_P}{LK_P^2 + K_P D + \mu_n^2 L D^2} \right|_D \quad (31)$$

This is relevant for a simple diffusion that is a core part of a more complex diffusion process in a battery.

5. Implementation of controls

Next, we apply the simple boundary control (27) on the detailed battery model. Although the control itself is simple, its mapping from the process state is rather complex; it involved the spatial and temporal dynamics of the main processes and several types of nonlinearities. The state to control mapping goes through Ohm's law in the solid and liquid phases, blockade of the electrodes

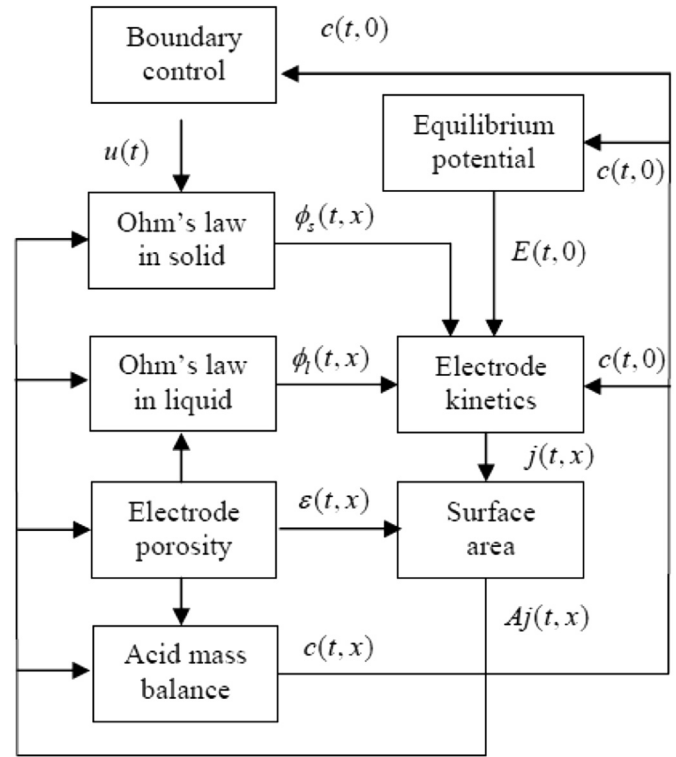


Fig. 4. The state to boundary control mapping.

(accounted for through the porosity and surface area), mass transfer of the acid ions in electrolyte and Butler–Volmer type exponential electrode kinetics and Nernst type logarithmic equilibrium potential as depicted in Fig. 4.

In practice, the depletion control (27) can be computed by (30) without concentration measurements at the boundary or approximated with two other controls (32) and (33). The simplest one (33) comes from approximation of the characteristic discharge curves with a simple empirical function. We reproduce the discharge curves in control simulation on the detailed model. The second control is a potentiostatic discharge (33). The latter is a widely used technique in practice that can be considered with certain reservation (explained in Section 6.5) as a simplified depletion control.

5.1. The empirical control

In practice, a simple approach can be applied. The control (27) is approximated with the two exponential functions

$$u_1(t) = -K_P(c_{\text{ref}} - c_d) \left(e^{-\tau_1 t} + k(e^{-\tau_2 t} - e^{-10^2 \tau_2 t}) \right) \quad (32)$$

in dependence on the two time constants τ_1, τ_2 (s^{-1}) and share k between exponents. These empirical parameters should be adjusted to the electrochemical processes in a battery under consideration.

In this work, we applied control (27) on the precise model of Section 2 and then we approximated the discharge current with (32). The empirical control (32) is the close approximation of the boundary control (27) with the reason that the latter control expressed in the logarithmic scale has two linear rising domains (Fig. 7), showing that two exponential functions are sufficient for approximation of the boundary controls with a simple time-dependent function. Also, the initial value of the function (32) is known from (27): $u_1(0) = -K_P(c_{\text{ref}} - c_d)$ and its zero asymptotic

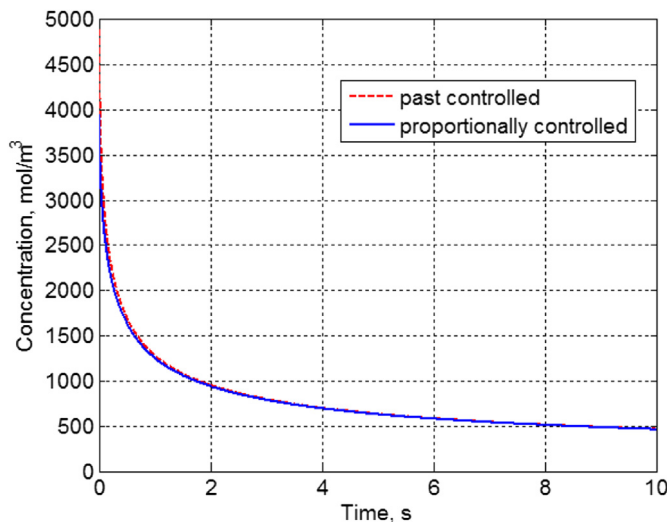


Fig. 3. The controlled processes on the boundary are almost identical when proportional and past controls are used.

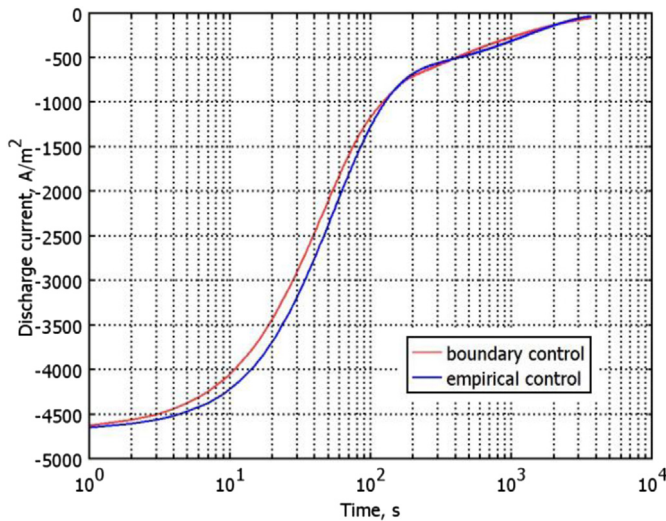


Fig. 5. The boundary control (27) is approximated with the simple empirical control (32) of two exponential functions.

behaviour is known $|u_1(t)|_D = 0$ if $t \rightarrow \infty$. Combined, these tell the form of function (32) and that only few constants are required for approximation of the boundary controls (27).

5.2. The potentiostatic control

In potentiostatic discharge, the electric current $u(t)$ is adjusted in a way that the potential $\phi_s(t, 0)$ is adjusted to the desired cell voltage ϕ_d on the collector of positive electrode

$$u(t) = -K_P(\phi_s(t, 0) - \phi_d) \quad (33)$$

Notice, that the control gain K_P has different units in the case of galvanostatic mass transfer control (m s^{-1}) and potentiostatic control ($\text{A m}^{-2} \text{V}^{-1}$). Also, their numerical values are different: the potentiostatic control gain is $2F$ times larger than the galvanostatic control gain.

If the desired voltage is selected close enough to the cut-off voltage, say $\phi_d = 1.75 \text{ V}$, the results are similar (Fig. 6) in the galvanostatic discharge control and potentiostatic discharge

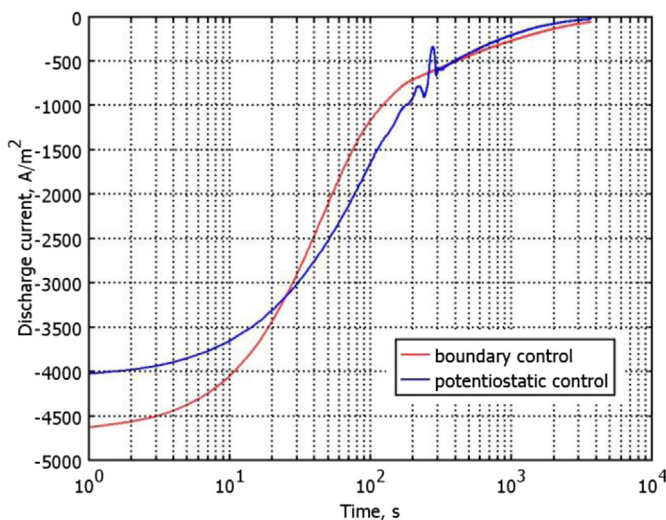


Fig. 6. The galvanostatic boundary control (27) and potentiostatic control (33) set to maintain 1.75 V.

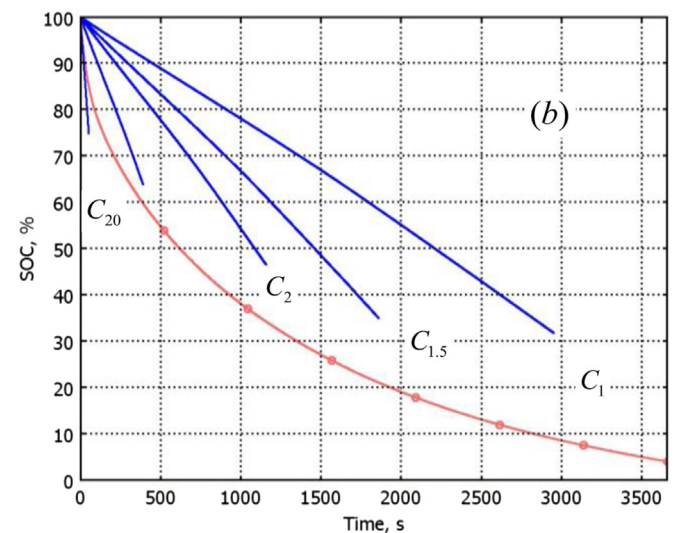
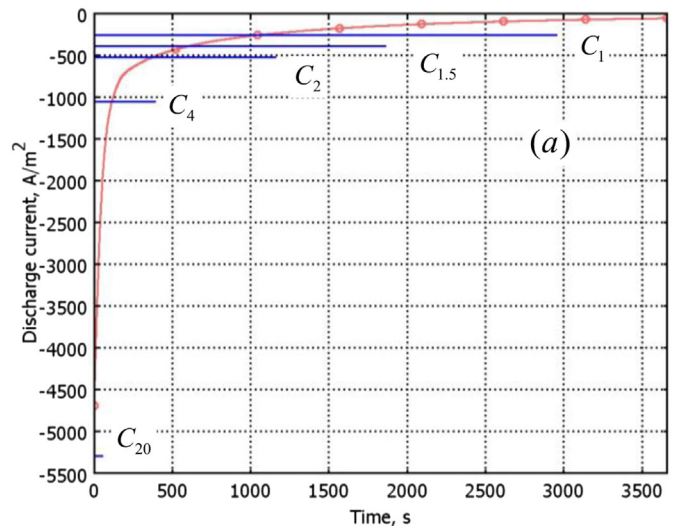


Fig. 7. The discharge current (a) and state of charge (b) in the cases of depletion control and constant current control at the loading rates C_{20} , C_4 , C_2 , $C_{1.5}$, C_1 . The stopping time (endpoint of the line) is infinite in the case of depletion control and essentially limited in the case of constant current control; only a fraction of charge can be withdrawn from battery with the constant current control.

control. This allows simple parameterisation of the empirical constants τ_1 , τ_2 , k in (32) of a real battery by the potentiostatic discharge curve. Some oscillation (Fig. 6) in the potentiostatic discharge curve emerges when the discharge current transfers from the fast-changing exponent to the slower one at ca 200–300 s; this is the same location where the concentration process in Fig. 11 reaches almost the zero level. This effect revealed in the simulation on the detailed model of Section 2 disappears if the desired voltage for potentiostatic control is set somewhat higher, say $\phi_d = 1.8 \text{ V}$.

In potentiostatic discharge, one has an essential risk to deplete the positive electrode from acid ions if the desired voltage is selected too close to the cut-off voltage. We return to this problem in Subsection 6.5.

6. Comparison of controls

In this section, we apply three different controls (27), (32) and (33) on the detailed battery model developed in Section 2.

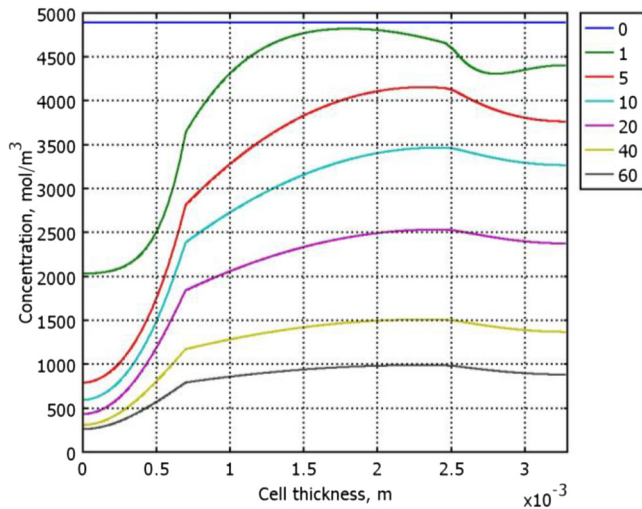


Fig. 8. The acid concentration in electrolyte at instances 0, 1, 5, 10, 20, 40 and 60 min. The electrolyte concentration at the collector of a positive electrode is upheld by the boundary control (27) at the desired level $c_d = 200 \text{ mol m}^{-3}$.

6.1. Constant discharge current

In constant loading, the depletion process of the positive electrode from the acid ions takes place, and the larger the discharge current is, the faster this occurs. As a result, a powerful discharge can be executed on a battery but only for a short period, and most of the chemical energy in the battery stays unused. After a certain period of rest, the loading process can be continued at a lower discharge current, so long as a new depletion takes place and this occurs many times. This is demonstrated in Fig. 7a for several loading rates C_{20} , C_4 , C_2 , $C_{1.5}$, C_1 . These rates per hour represent the discharge currents (A) per battery capacity (Ah). For instance, C_{20} is the fast discharge rate during aimed 1/20 h and C_1 is the slow discharge rate in one hour. These rates in Fig. 7b reveal that the discharge process ends far before the chemical energy is withdrawn from the battery. For further withdrawal of 75–32% energy, the battery must stay at rest. Interruption of the power supply that occurs is not generally accepted in backup systems. Therefore, other

discharge strategies should be applied that maximise the discharge power without interruption.

6.2. Refining the depletion process

The loading rates in other units (capacity per area) represent the discharge current density. For instance, the current density $i_{app} = 5291 \text{ A m}^{-2}$ is relevant to the loading rate C_{20} at 20 times the battery capacity 60 A per cell total area 0.2268 m^2 shown in Fig. 7a, and the battery state of charge in Fig. 7b. In this case, the stopping time when depletion occurs is 60 s, and only 25% of the available energy $3.2 \times 10^5 \text{ As m}^{-2}$ is reached in loading of the battery (i.e. SOC = 75%). With less discharge current, more withdrawal of energy can be reached at the expense of less power for use. For instance, the discharge current $i_{app} = 264 \text{ A m}^{-2}$ at loading rate C_1 allows reaching 68% of energy $8.7 \times 10^5 \text{ As m}^{-2}$ use, but the discharge current 264 A m^{-2} is much lower in this case. The proposed depletion control (27) gives a refined balance between energy and discharge current.

6.3. Galvanostatic depletion control

The boundary control (27) aimed at $c_d = 200 \text{ mol m}^{-3}$ (i.e. 4% of the reference concentration) with control gain $K_p = 1.0 \text{ m s}^{-1}$ allows uninterrupted power supply that gradually declines from the maximum current at $2FK_p(c_{ref} - c_d)$ to zero when the battery becomes discharged completely. The corresponding discharge current and SOC are shown in Fig. 7a and b, correspondingly.

In depletion control, the ion concentration of electrolyte changes in a way that the positive electrode is not depleted from acid (Fig. 8). The ion concentration reaches about the desired level at the collector of the positive electrode. The desired level can be reached faster and closer with the bigger control gain K_p in a less smooth battery control. In any case, the concentration reaches a steady level when the current approaches zero.

In depletion control, the cell voltage $V_{cell} = \phi_s(t, 0)$ between the electrodes, at first, drops lower and then partly recovers, and then gradually declines as far as it reaches the cut-off voltage when the current reached zero (Fig. 9). Though unlikely, the thermodynamic

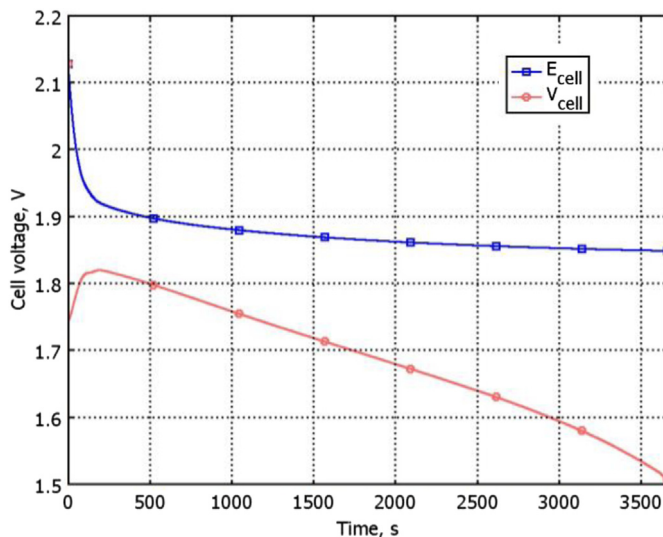


Fig. 9. The voltage between electrodes (V_{cell}) and the equilibrium voltage (E_{cell}) of cell during depletion control.

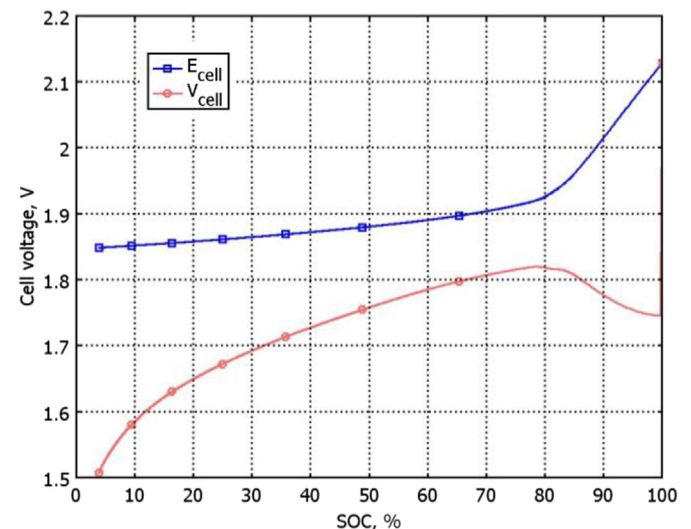


Fig. 10. The voltage between electrodes (V_{cell}) and the equilibrium voltage (E_{cell}) in dependence on state of charge (SOC).

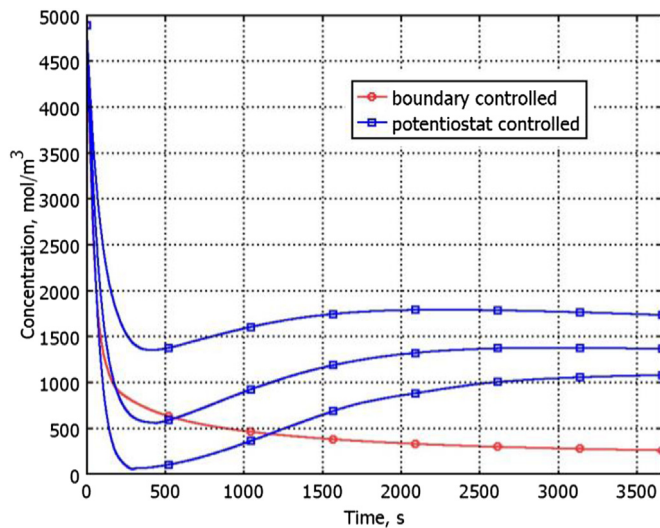


Fig. 11. The ion concentration of electrolyte at the collector of positive electrode controlled with the boundary control (27) and potentiostatic control (33) set to maintain 1.75 (lowest curve), 1.8 and 1.85 V. The boundary control is set at $c_d = 200 \text{ mol m}^{-3}$.

equilibrium potential $E_{\text{cell}} = E_{\text{PbO}_2} - E_{\text{Pb}}$ decreases monotonically during the depletion control. The difference between these two voltages $V_{\text{cell}} - E_{\text{cell}}$ is the electromotive force of cell or overpotential that has the minimum value shortly after (ca. 300 s) the depletion control is started. This represents a certain relaxation in overpotential that takes place when the concentration value reaches the control target $c_d = 200 \text{ mol m}^{-3}$ in Fig. 8.

This relaxation in a short period loses its effect later, at first gradually and then more rapidly. The rapid change at the end of discharge shown in dependence on the state of charge (Fig. 10) is acquainted, but the relaxation process initially seemed novel in batteries control.

6.4. The empirical depletion control

The empirical depletion process control (32) specified for the battery of this case study, with three empirical constants $\tau_1 = 2 \times 10^{-2} \text{ s}^{-1}$, $\tau_2 = 8 \times 10^{-4} \text{ s}^{-1}$, $k = 0.15$ (dim less) is in good agreement (Fig. 5) with the boundary control (27).

6.5. The potentiostatic (depletion) control

The potentiostatic discharge (33) is a simple alternative for the depletion control; however, it may cause premature electrode depletion if the desired voltage is selected too close to the cut-off voltage. This is demonstrated in Fig. 11 with several desired voltages $\phi_d = 1.75, 1.8, 1.85 \text{ V}$ that this is not a safe mode to control if the desired voltage for the potentiostatic control is selected somewhat lower than $\phi_d = 1.75 \text{ V}$, because the acid concentration then drops to zero, which depletes the electrode from ions and the current flow ends in a few minutes. This premature electrode starvation can be prevented with the depletion control (27) as shown in Fig. 11.

6.6. The advantage and disadvantage of controls

The potentiostatic discharge is the most simple and practical control however not a safe mode when the set-point voltage is selected too close to the cut-off voltage, i.e., when one aims a too low concentration level in the electrolyte he/she ends up in

starvation of the positive electrode. In contrast, the galvanostatic discharge is a safe depletion control mode but also a model-based control that uses a simplified model and its parameters L and D must be calibrated to the specific type of batteries applied in discharge. Evidently this control is less fitting for practice than the former potentiostatic control. Also the empirical control requires adjustment of the parameters τ_1 , τ_2 and k to the batteries. The potentiostatic discharge if applied beforehand for testing helps to calibrate the empirical battery model by the potentiostatic discharge curve. Three galvanostatic depletion controls are considered in this paper named as the proportional and past controls, and the feed-forward control. These are basically the same controls represented in different forms. Two of them (proportional and past) are feedback controls; they tolerate model uncertainties. The proportional control depends on the electrolyte concentration measurements in the positive electrode and therefore is impractical. The past control is applicable in practice; it depends on the current and past discharge current measurements.

7. Conclusion

The depletion process in a battery can be controlled using exponentially stabilising boundary controls that ensure uninterrupted power supply at the maximum current level that is relevant to the physics of a non-depleted electrode. In practice, the boundary control can be either approximated with simpler empirical controls or with integrated past controls that do not require acid concentration measurements at the boundary.

The depletion control developed for a lead-acid battery can be modified relatively simply for other types of batteries like a lithium-ion battery.

Appendix

Table 1

List of parameter values.

Symbol	Region in cell				Unit
	1	2	3	4	
a_{max}	2.3×10^7			2.3×10^6	$\text{m}^2 \text{m}^{-3}$
b	1.2×10^{-5}			1.05×10^{-5}	$\text{m}^3 \text{mol}^{-1} \text{V}^{-1}$
c_d	200				mol m^{-3}
c_{ref}	4890				mol m^{-3}
D	$1.75 \times 10^{-9} + 2.6 \times 10^{-13} c$				$\text{m}^2 \text{s}^{-1}$
i_0	0.003			0.03	A m^{-2}
K_p	1.0				m s^{-1}
	1.9×10^5				$\text{A m}^{-2} \text{V}^{-1}$
t_0^+	0.72				$\text{m}^3 \text{mol}^{-1}$
V_e	45×10^{-6}				$\text{m}^3 \text{mol}^{-1}$
V_o	17.5×10^{-6}				$\text{m}^3 \text{mol}^{-1}$
V_{Pb}	18.3×10^{-6}				$\text{m}^3 \text{mol}^{-1}$
V_{PbO_2}	24.7×10^{-6}				$\text{m}^3 \text{mol}^{-1}$
V_{PbSO_4}	48.1×10^{-6}				$\text{m}^3 \text{mol}^{-1}$
U	1.67			−0.336	V
α_a	1.21			1.55	—
α_c	0.79			0.45	—
β_1	0.5			0.5	—
β_2	1.5	1.5	3.53	1.5	—
β_3	2			2	—
β_4	1.06			1.06	—
ε		1	0.73		—
ε_{max}	0.53			0.53	—
ε_{min}	0.3466			0.3066	—
ϕ_d	1.75				V
κ	$-1.88 + 0.047c - 6 \times 10^{-6} c^2$				S m^{-1}
σ	4.8×10^5			8000	S m^{-1}
l_i	0.07	0.176	0.006	0.05	cm

Table 2

List of symbols.

Symbol	Description	Unit
A	Active surface area per unit volume of porous electrode	$\text{m}^2 \text{m}^{-3}$
a_{max}	Maximum active surface area per unit volume of porous electrode	$\text{m}^2 \text{m}^{-3}$
c	Concentration of acid in electrolyte	mol m^{-3}
C_x	Loading rate: battery capacity (Ah) per discharge current $i_{\text{app}} = x$ (A)	h
c_d	Desired (target) concentration at collector of the positive electrode	mol m^{-3}
c_{ref}	Reference (initial) concentration	mol m^{-3}
D	Diffusivity of acid ions	mol m^{-2}
E	Equilibrium potential of reaction in positive or negative electrode	V
F	Faraday's constant, 96487	C mol^{-1}
i_0	Exchange current density	A m^{-2}
i_{app}	Applied current density	A m^{-2}
i_l	Current density in electrolyte	A m^{-2}
j	Current density in transfer from electrolyte to solid matrix	A m^{-2}
K_p	Control gain: galvanostatic or potentiostatic	m s^{-1} , $\text{A m}^{-2} \text{V}$
L	Positive electrode thickness: $L = l_1$	m
l_i	Layer thickness	m
R	Universal gas constant, 8.3145	$\text{J mol}^{-1} \text{K}^{-1}$
T	Temperature (standard)	K
t_0^+	Transference number: share of total currents carried by H^+ ions	—
U	Standard equilibrium potential of reaction in positive/negative electrode vs. H_2 electrode	V
u	Boundary control: current density i_{app}	A m^{-2}
u_1	Boundary control: mass flux	$\text{mol m}^{-3} \text{s}^{-1}$
u_v	Convection volume average velocity	m s^{-1}
z	Electrochemical state (vector)	Depends
V_i	Particle molar volume of species i in liquid: water (e), acid (o) and solid (Pb, PbO_2 , PbSO_4)	$\text{m}^3 \text{mol}^{-1}$
α_a	Anodic charge transfer coefficient	—
α_c	Cathodic charge transfer coefficient	—
β_1	Efficiency exponent for electric conductivity in the porous media	—
β_2	Efficiency exponent for liquid phase transport in the porous media	—
β_3	Morphology exponent for SOC	—
ε	Volume fraction filled with acid: porosity	—
ε_{max}	Porosity in the fully charged electrode	—
ε_{min}	Porosity in the zero charged electrode	—
ϕ_d	Desired (reference) voltage in potentiostatic control	V
ϕ_l	Electrolyte potential	V
ϕ_s	Solid matrix potential	V
η	Overpotential	V
θ	State of charge, SOC	—
κ	Electrolyte conductivity	S m^{-1}
σ	Conductivity of positive or negative electrode	S m^{-1}

References

- [1] J. Newman, W.H. Tiedemann, *AIChE J.* 21 (1975) 25–41.
- [2] H. Gu, T.V. Nguyen, R.E. White, *J. Electrochem. Soc.* 134 (12) (1987) 2953–2960.
- [3] T.V. Nguyen, R.E. White, H. Gu, *J. Electrochem. Soc.* 137 (10) (1990) 2998–3004.
- [4] W.B. Gu, C.Y. Wang, B.Y. Liaw, *J. Electrochem. Soc.* 144 (1997) 2053–2061.
- [5] J. Newman, K. Thomas-Alyed, *Electrochemical Systems*, John Wiley & Sons, New Jersey, 2004.
- [6] V. Boovaragavan, R.N. Methakar, V. Ramadesigan, V.R. Subramanian, *J. Electrochem. Soc.* 156 (11) (2009) A854–A862.
- [7] M. Cugnet, S. Laruelle, S. Grugeon, B. Sahut, J. Sabatier, J.-M. Tarascon, A. Oustaloup, *J. Electrochem. Soc.* 156 (12) (2009) A974–A985.
- [8] A.G. Kashkooli, F. Siamak, A.S. Fung, Z. Chen, *Electrochim. Acta* 97 (2013) 278–288.
- [9] D. Berndt, *Maintenance-free Batteries*, Research Studies Press Ltd., John Wiley & Sons Inc, 1997.
- [10] A. Tenno, T. Suntio, R. Tenno, *J. Power Sources* 103 (2001) 42–53.
- [11] A. Tenno, in: *Proc. EuroPES 2002 Greece*, 2002, pp. 554–562.
- [12] A. Tenno, R. Tenno, T. Suntio, *J. Electrochem. Soc.* 151 (6) (2004) A806–A824.
- [13] A. Tenno, R. Tenno, T. Suntio, *J. Power Sources* 158 (2) (2006) 1029–1033.
- [14] R. Tenno, *Int. J. Control* 84 (9) (2011) 1522–1534.
- [15] R. Tenno, A. Pohjoranta, *IFAC J. Process Control* 25 (1) (2012) 262–265.
- [16] R. Tenno, A. Pohjoranta, in: *Proc. IFAC 19th World Congress Cape Town*, 24–29 August, 2014, p. 6.
- [17] A. Pohjoranta, R. Tenno, *J. Math. Chem.* 25 (5) (2014) 1414–1440.
- [18] R. Tenno, *IFAC J. Process Control* 24 (1) (2014) 82–92.
- [19] J. Newman, W.H. Tiedemann, *J. Electrochem. Soc.* 144 (9) (1997) 3081–3091.
- [20] A. Tenno, R. Tenno, T. Suntio, *J. Power Sources* 111 (2002) 65–82.
- [21] W.B. Gu, G.Q. Wang, C.Y. Wang, *J. Power Sources* 108 (2002) 174–184.
- [22] R. Curtain, H. Zwart, *An Introduction to Infinite-dimensional Linear Systems Theory*, Springer-Verlag, 1995.
- [23] F. Tröltzsch, *Optimal Control of Partial Differential Equations. Theory, Methods and Applications*, American Mathematical Society, Providence, RI, 2010.
- [24] A. Bensoussan, G. Da Prato, M.C. Delfour, S.K. Mitter, *Representation and Control of Infinite Dimensional Systems*, in: *Systems & Control: Foundations & Applications*, Birkhäuser, Boston Inc., Boston, MA, 2007.
- [25] R. Tenno, *IFAC J. Process Control* 24 (7) (2014) 1098–1105.